# Rate processes with dynamical disorder: A direct variational approach

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# Rate processes with dynamical disorder: A direct variational approach

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Using path integral approach, we develop variational approximations to the calculation of survival probability for rate processes with dynamical disorder. We derive both upper and lower bounds to the survival probability using Jensen's inequality. The inequalities involve the use of a trial action for which the path integrals can be evaluated exactly. Any parameter in the trial action can be varied to optimize the bounds. We have also derived a lower bound to the rate of the process. As a simple illustration, we apply the method to the problem of a particle undergoing Brownian motion in a harmonic potential well, in the presence of a delta function sink, for which one can calculate the exact survival probability numerically. The calculation confirms the two inequalities. The method should be very useful in similar but more complex problems where even numerical solution is not possible. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2200695]

## I. INTRODUCTION

Problems in chemical and biological physics often involve reactions occurring in a fluctuating environment as has been pointed out in an interesting review by Zwanzig.[1] The concentration $C$ of a species changes according to the equation $dC/dt=-k(B)C$, where the rate constant $k(B)$ depends on the control parameter $B$ which often is a random function of time. This is referred to as a rate process with dynamical disorder and is of interest in the theory of spectral line shapes, self-diffusion in water, gated diffusion, protein dynamics, fluorescence depolarization, dynamical percolation, barrierless relaxation etc. Though one can formally write $C(t)=e^{-\int_0^t k(B(s))ds}C(0)$, calculation of average value $\langle C(t)\rangle$ over all realizations of the random function $B(s)$ is an incredibly tough problem. Direct calculations of this average would normally involve lengthy computer simulations.[2] Therefore Zwanzig[1] recommends an indirect approach in which he starts with a stochastic Liouville equation. Averaging over the noise one can get a Fokker-Planck equation which may then be solved to get $\langle C(t)\rangle$.

The first approach to the calculation of rates was the Wilemski-Fixman[3,4] (WF) closure approximation, which was applied to reaction dynamics in polymers. The closure approximation requires the initial distribution to be the equilibrium one. Soon after it was suggested, Doi[5] showed that it could be derived from a variational upper bound on the Laplace transform of the survival probability. In an interesting paper, Portman and Wolynes[6] have studied variational approximations to the calculation of survival probability. They have found upper and lower bounds for the Laplace transform of the survival probability. From this, they also obtain bounds on the mean first passage time. The bounds are valid only if the initial distribution is the equilibrium one. It has been pointed out that the mean reaction time approach is not adequate for nonequilibrium initial conditions.[7] Bounds on the survival probability itself would be much more useful than bounds on its Laplace transform. Further, one would like them to be valid even when the starting probability distribution is a nonequilibrium one. In this paper, we adopt the direct approach and using path integrals, we show how one can develop a variational approach to the calculation of the rate and survival probability, for arbitrary initial conditions. Direct approaches have been pursued earlier in a series of interesting papers by the group of Wolynes.[8–10] Wang and Wolynes[8] have included non-Markovian fluctuation through a path integral approach. The path integrals may be evaluated approximately using "dominant survival paths." They also show that in some situations "instanton like" contributions are important in the calculation of survival probability.[10] To illustrate our approach, we make use of a simple one dimensional problem. The method is applicable and is hopefully more useful for multidimensional problems in which even numerical solutions are difficult to obtain. Such applications will be presented in a future publication.

## II. DIFFUSIONAL MOTION IN THE PRESENCE OF A SINK

The probability density $P(x,t)$ for a particle undergoing diffusional motion in one dimension subjected to a potential $V(x)$ and decaying with a position dependent rate constant $k(x)$ is described by the equation[11–16]

$$\frac{\partial P(x,t)}{\partial t}=\left\{D\frac{\partial^2}{\partial x^2}+\frac{\partial}{\partial x}\frac{dV(x)}{dx}-k(x)\right\}P(x,t). \tag{1}$$

The solution to this can be written as a path integral. If the particle was initially at $x_0$ at the time $t=0$, then the probability of finding the particle at $x_T$ at the time $T$ is given by the path integral

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$$G(x_T,T|x_0,0)=\int_{(0,x_0)}^{(T,x_T)}\mathcal{D}x(s)\exp\left(-A_0[x(s)]-\int_0^T k(x(s))ds\right), \tag{2}$$

with $A_0[x(s)]=1/4D\int_0^T(dx(s)/ds+dV(x)/dx)^2ds$.[17] The measure of the path integral is chosen such that if there is no absorption $[k(x)=0]$, then $\int dx_T G(x_T,T|x_0,0)=1$. If the initial distribution of the particle is $P_0(x_0)$ at $t=0$, then the survival probability after time $T$ is

$$P(T)=\int dx_T\int dx_0 G(x_T,T|x_0,0)P_0(x_0), \tag{3}$$

which may be written as

$$P(T)=\int dx_T\int dx_0 P_0(x_0)\int_{(0,x_0)}^{(T,x_T)}\mathcal{D}x(s)\exp(-A[x(s)]), \tag{4}$$

where $A[x(s)]=A_0[x(s)]+\int_0^T k(x(s))ds$.

It is convenient to introduce the short hand notation

$$\langle M\rangle_{\tilde{A},T}=\frac{\int dx_T\int dx_0 P_0(x_0)\int_{(0,x_0)}^{(T,x_T)}\mathcal{D}x(s)\exp(-\tilde{A}[x(s)])M[x(s)]}{\int dx_T\int dx_0 P_0(x_0)\int_{(0,x_0)}^{(T,x_T)}Dx(s)\exp(-\tilde{A}[x(s)])}, \tag{5}$$

where $M[x(s)]$ can be any functional of $x(s)$ and $\tilde{A}[x(s)]$ denotes any given "action." With this notation,

$$P(T)=\left\langle\exp\left(-\int_0^T k(x(s))ds\right)\right\rangle_{A_0,T}. \tag{6}$$

## III. THE LOWER BOUNDS

### A. On the survival probability

The averaging in Eq. (6) is difficult to perform. Let us therefore assume that we have a trial action $A_{\rm tr}$. Equation (6) can be written as

$$P(T)=\langle\exp(-\Delta A[x(s)])\rangle_{A_{\rm tr},T}\times\int dx_T\int dx_0 P_0(x_0)\int_{(0,x_0)}^{(T,x_T)}\mathcal{D}x(s)\exp(-A_{\rm tr}[x(s)]),$$

where $\Delta A[x(s)]=A[x(s)]-A_{\rm tr}[x(s)]$. This may be rewritten as

$$P(T)=\langle\exp(-\Delta A[x(s)])\rangle_{A_{\rm tr},T}P_{\rm tr}(T).$$

where $P_{\rm tr}(T)$ is the survival probability if the time development of the system is governed by the action $A_{\rm tr}[x(s)]$. Now we use Jensen's inequality[18,19] for exponential functions (i.e., $\langle e^{-x}\rangle\geq e^{-\langle x\rangle}$) and get

$$P(T)\geq\exp(-\langle\Delta A[x(s)]\rangle_{A_{\rm tr},T})P_{\rm tr}(T). \tag{7}$$

The above result is valid for any arbitrary but well behaved trial action. If the trial action depends on a parameter $\lambda$, then the parameter can be varied to get the maximum value of the right hand side of Eq. (7) and even that will be a lower bound on the survival probability.

A different way of proceeding gives another lower bound. We define a different average, $\langle M\rangle_{\tilde{A},T,x_0}$, by

$$\langle M\rangle_{\tilde{A},T,x_0}=\frac{\int dx_T\int_{(0,x_0)}^{(T,x_T)}\mathcal{D}x(s)\exp(-\tilde{A}[x(s)])M[x(s)]}{\int dx_T\int_{(0,x_0)}^{(T,x_T)}Dx(s)\exp(-\tilde{A}[x(s)])}. \tag{8}$$

This average is calculated over all paths that start with the same initial position $x_0$ at the time $t=0$. Then

$$P(T)=\int dx_0 P_0(x_0)<\exp(-\Delta A)>_{A_{\rm tr},T,x_0}P_{{\rm tr},x_0}(T), \tag{9}$$

$$P(T)\geq\int dx_0 P_0(x_0)\exp(-<\Delta A>_{A_{\rm tr},T,x_0})P_{{\rm tr},x_0}(T). \tag{10}$$

$P_{{\rm tr},x_0}(T)$ is the survival probability for the trial action $A_{\rm tr}$, if the particle started at $x_0$. It can be calculated from Green's function $G_{\rm tr}(x_T,T|x_0,0)$, which is the probability of finding the particle at $x_T$ at the time $T$, given that it started at $x_0$ at the time 0 and that the time development is governed by the action $A_{\rm tr}$. It is given by the expression $P_{{\rm tr},x_0}(T)=\int dx_T G_{\rm tr}(x_T,T|x_0,0)$.

If one chooses $A_{\rm tr}$ to be $A_0$ itself, then the trial action contains no sink term. In that case first $P_{{\rm tr},x_0}(T)=1$ and Eq. (10) becomes

$$P(T)\geq\int dx_0 P_0(x_0)\exp\left(-\int_0^T ds\langle k(x(s))\rangle_{A_{\rm tr},x_0}\right). \tag{11}$$

The term on the right hand side of Eq. (10) is the first order inhomogenous cumulant expansion and one gets the inequality of Yang and Cao.[20,21] Notice, however, that our inequality in Eq. (7) is more general and that the inequality pointed out by them is a special case. Applying Jensen's inequality once

more to the right hand side of Eq. (10), we get

$$\int dx_0 P_0(x_0)\exp(-\langle \Delta A\rangle_{A_{\rm tr},T,x_0})P_{{\rm tr},x_0}(T) \geqslant P_{\rm av} \times\exp\left(-\frac{1}{P_{\rm av}}\int dx_0 P(x_0)\langle \Delta A\rangle_{A_{\rm tr},T,x_0}P_{{\rm tr},x_0}(T)\right), \tag{12}$$

where $P_{\rm av}=\int dx_0 P(x_0)P_{{\rm tr},x_0}(T)$. Thus

$$P(T) \geqslant P_{\rm av}\exp\left(-\frac{1}{P_{\rm av}}\int dx_0 P(x_0)\langle \Delta A\rangle_{A_{\rm tr},T,x_0}P_{{\rm tr},x_0}(T)\right). \tag{13}$$

Obviously the inequality of Eq. (10) is better than the one of Eq. (13).

It is interesting to ask what would the long time behavior of the lower bound be. We analyze this in the Appendix and show that for long times, the lower bound decays exponentially.

### B. On the rate

$R(T)$, the rate of change of $P(T)$, is defined by

$$R(T) = -\frac{dP(T)}{dT} = \int dx_T k(x_T)\int dx_0 G(x_T,T|x_0,0)P_0(x_0) = \int dx_T k(x_T)\int dx_0\int_{0,x_0}^{T,x_T}\mathcal{D}x(s)e^{-A[x(s)]}P_0(x_0) = \langle\langle e^{-(A-A_{\rm tr})}\rangle\rangle_{A_{\rm tr},T}R_{\rm tr}(T), \tag{14}$$

where we have introduced the notation

$$\langle\langle M[x(s)]\rangle\rangle_{A_{\rm tr},T} = \frac{\int dx_T k(x_T)\int dx_0 P_0(x_0)\int_{0,x_0}^{T,x_T}\mathcal{D}x(s)M[x(s)]e^{-A_{\rm tr}}}{\int dx_T k(x_T)\int dx_0 P_0(x_0)\int_{0,x_0}^{T,x_T}\mathcal{D}x(s)e^{-A_{\rm tr}}}. \tag{15}$$

Then the rate given in Eq. (14) may be written as

$$R(T) = \langle\langle \exp(-\Delta A[x(s)]\ )\rangle\rangle_{A_{\rm tr},T}R_{\rm tr}(T), \tag{16}$$

where

$$R_{\rm tr}(T) = \frac{\int dx_T k(x_T)\int dx_0\int_{0,x_0}^{T,x_T}Dx(s)e^{-A_{\rm tr}[x(s)]}P_0(x_0)}{\int dx_T\int dx_0\int_{0,x_0}^{T,x_T}Dx(s)e^{-A_{\rm tr}[x(s)]}P_0(x_0)} \tag{17}$$

is the rate calculated using the trial action $A_{\rm tr}$. Using Jensen's inequality again, we get

$$R(T) \geqslant R_{\rm tr}(T)\exp(-\langle\langle \Delta A[x(s)]\rangle\rangle_{A_{\rm tr},T}), \tag{18}$$

which is a lower bound on the rate of the reaction at the time $T$. Another bound similar to Eq. (10) can also be obtained. One gets

$$R(T) \geqslant \int dx_0 P_0(x_0)R_{{\rm tr},x_0}(T)P_{{\rm tr},x_0}, \tag{19}$$

where

$$R_{{\rm tr},x_0}(T) = \frac{\int dx_T k(x_T)\int_{0,x_0}^{T,x_T}Dx(s)e^{-A_{\rm tr}[x(s)]}}{\int dx_T\int_{0,x_0}^{T,x_T}Dx(s)e^{-A_{\rm tr}[x(s)]}}. \tag{20}$$

## IV. THE UPPER BOUND

To find an upper bound to the survival probability, we start by replacing $T$ by $t$ in Eq. (16) to get

$$R(t) \geqslant \exp(-\langle\langle \Delta A\rangle\rangle_{A_{\rm tr},t})R_{\rm tr}(t). \tag{21}$$

Therefore, the survival probability

$$P(T) = 1-\int_0^T dtR(t) \leqslant 1-\int_0^T dte^{-\langle\langle \Delta A\rangle\rangle_{A_{\rm tr},t}}R_{\rm tr}(t). \tag{22}$$

Combining the two equations (7) and (22) we can write

$$1-\int_0^T dte^{-\langle\langle \Delta A\rangle\rangle_{A_{\rm tr},t}}R_{\rm tr}(t) \geqslant P(T) \geqslant \exp(-\langle \Delta A\rangle_{A_{\rm tr},T})P_{\rm tr}(T).$$

It is obvious that the above inequalities, though written for the case of a one dimensional problem, are applicable to the calculation of survival probability or rate in any number of dimensions.

## V. DIFFUSION IN A HARMONIC POTENTIAL

As a simple illustration of the utility, we take the one dimensional diffusive motion under the potential $V(x)=1/2\alpha x^2$. In this case

$$A[x(s)] = \frac{1}{4D}\left(\int_0^T\left\{\frac{dx(s)}{ds}+\alpha x(s)\right\}^2 ds\right)+\int_0^T k(x(s))ds.$$

We take the sink function $k(x)$ to be a Dirac delta function with strength $k_0$,[11–13] and write it as $k(x)=k_0\delta(x-x_s)$. For this choice of the sink, the survival probability can be calculated

exactly.[11,13] Interestingly, the Wilemski-Fixman approach, though approximate, leads to the exact answer for the Laplace transform of the survival probability if the initial probability distribution is the equilibrium one in the absence of the sink.[20] In our approach, we need a trial action, which we take to be one with quadratic sink given by

$$A_{\rm tr}[x(s)] = \frac{1}{4D}\left\{\int_0^T \left(\frac{dx(s)}{ds} + \alpha x(s)\right)^2\right\} + \int_0^T k_{\rm tr} x^2(s) ds,$$

where $k_{\rm tr}$ is a variational parameter. Green's function for this action is

$$G_{\rm tr}(x_T, T|x_0, 0) = \sqrt{\frac{e^{T\alpha}\alpha_s \operatorname{csc} h[T\alpha_s]}{4\pi D}} \exp\left(\frac{(x_0^2 - x_T^2)\alpha - (x_0^2 + x_T^2)\alpha_s \coth[T\alpha_s] + 2x_0 x_T \alpha_s \operatorname{csc} h[T\alpha_s]}{4D}\right), \tag{23}$$

where $\alpha_s = \sqrt{\alpha^2 + 4Dk_{\rm tr}}$. Using the above, we have calculated bounds for survival probability. If the initial distribution is given by $P_0(x_0) = e^{-x_0^2/2\sigma^2}/\sigma\sqrt{2\pi}$, then $P_{\rm tr}(T)$ can be analytically calculated and the result is

$$P_{\rm tr}(T) = \frac{\sqrt{2\alpha_s D e^{T\alpha} \operatorname{csc} h[T\alpha_s]}}{\sqrt{2D(\coth[T\alpha_s]\alpha_s + \alpha) + (-\alpha^2 + \alpha_s^2)\sigma^2}}.$$

One also finds

$$\langle \Delta A \rangle_{A_{\rm tr}, T} = \frac{1}{P_{\rm tr}(T)}\left(k_{\rm tr}\int dx_T \int dx_0 P_0(x_0) \int_0^T dy y^2 G_{\rm tr}(x_T, T|y, s) G_{\rm tr}(y, s|x_0, 0) ds - k_0 \int dx_T \int dx_0 P_0(x_0) \right.$$
$$\left. \times \int_0^T ds G_{\rm tr}(x_T, T|x_s, s) G_{\rm tr}(x_s, s|x_0, 0)\right) \tag{24}$$

and

$$\langle\langle \Delta A \rangle\rangle_{A_{\rm tr}, t} = \frac{1}{\int dx_0 P_0(x_0) G_{\rm tr}(x_s, t|x_0, 0)}\left(k_0 \int_0^t dt_1 \int dx_0 P_0(x_0) \times G_{\rm tr}(x_s, t|x_s, t_1) G_{\rm tr}(x_s, t_1|x_0, 0)\right.$$
$$\left. - k_{\rm tr}\int_0^t dt_1 \int dx_0 P_0(x_0) \int y^2 dy G_{\rm tr}(x_s, t|y, t_1) G_{\rm tr}(y, t_1|x_0, 0)\right). \tag{25}$$

Similarly

$$R_{\rm tr}(t) = \frac{\sqrt{e^{t\alpha}\alpha_s \operatorname{csc} h[t\alpha_s]}}{\sqrt{2\pi(2D - \sigma^2(\alpha - \alpha_s \coth[t\alpha_s]))}} e^{-x_s^2(2D\alpha + (-\alpha^2 + \alpha_s^2)\sigma^2 + 2D\alpha_s \coth[t\alpha_s])/4D(2D - \sigma^2(\alpha - \alpha_s \coth[t\alpha_s]))}.$$

The averages in Eqs. (24) and (25) are easy to evaluate as the position integrations are all Gaussian. The integral over time has to be evaluated numerically.

We have done similar calculations with trial action having two parameters. The two parameter trial action is

$$A_{\rm tr}[x(s)] = \frac{1}{4D}\left\{\int_0^T \left(\frac{dx(s)}{ds} + \alpha x(s) + \gamma\right)^2\right\} + \int_0^T k_{\rm tr}\left(x(s) + \frac{\gamma}{\alpha}\right)^2 ds,$$

and Green's function for this action is

$$G_{\rm tr}(x_T, T|x_0, 0) = \sqrt{\frac{e^{T\alpha}\alpha_s \operatorname{csc} h[T\alpha_s]}{4\pi D}} \times e^{(x_0 - x_T)(x_0\alpha + x_T\alpha + 2\gamma) - ((x_0 + \gamma/\alpha)^2 + (x_T + \gamma/\alpha)^2)\alpha_s \coth[T\alpha_s] + 2(x_0 + \gamma/\alpha)(x_T + \gamma/\alpha)\alpha_s \operatorname{csc} h[T\alpha_s]/4D}. \tag{26}$$

Using the above expressions, the bounds in Secs. III and IV were evaluated using MATHEMATICA. In order to find how good the approximations are, we also did exact calculations by solving Eq. (1) numerically using the discrete variable representation (DVR) method.[22] Calculations were done for the parameter values $\alpha = 2$, $D = 2$, $k = 1.25$, and $x_s = 2$. For these, we took two initial probability distributions, viz., one having $\sigma = 1$ (the equilibrium distribution in the absence of the sink) and another with $\sigma = 0.5$ (which would be a non-equilibrium one if there was no sink). The lower bounds to the survival probability were found using Eq. (7). Use of Eq. (10) is more tedious, as one now has to perform integration over $x_0$ numerically. On calculation, we found that this bound is lower than the one in Eq. (7), but not significantly

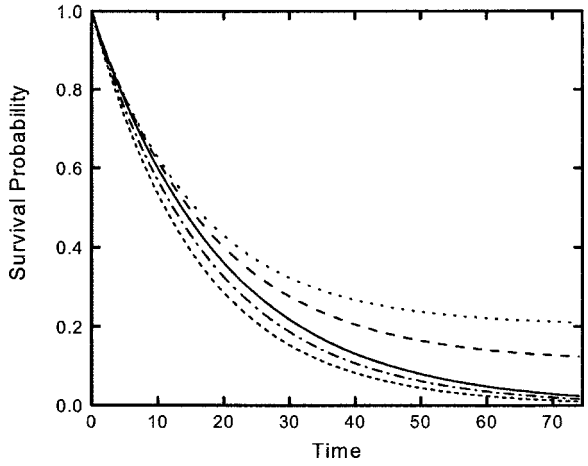


FIG. 1. The exact and optimized lower and upper bounds to the survival probability plotted against time. The one parameter upper bound (dotted line), two parameter upper bound (dashed line), one parameter lower bound (short dashed line), two parameter lower bound (dot-dashed line), and the exact (solid line) are shown. The exact survival probability lies between the bounds. The values of the parameters used were $\alpha=2$, $D=2$, $x_s=2$, $k=1.25$, and $\sigma=1$.

(difference was less than 1%) and therefore, we report calculations using only Eq. (7). The survival probabilities for these two different cases are shown in Figs. 1 and 2. Results of calculations with two trial parameters $(k_{tr}, \gamma)$ too are given in the figures. Note that the parameters $(k_{tr}, \gamma)$ depend on the value of $T$. It is clear that the method leads to survival probabilities close to the exact ones.

Calculations of upper bound were performed using a one parameter $(k_{tr})$ and two parameter trial actions $(k_{tr}, \gamma)$ and the result from the two parameter calculation is found to be significantly better than the one parameter results. However, the upper bound has the defect that $P(T)$ approaches a finite nonzero value as $T\to\infty$.

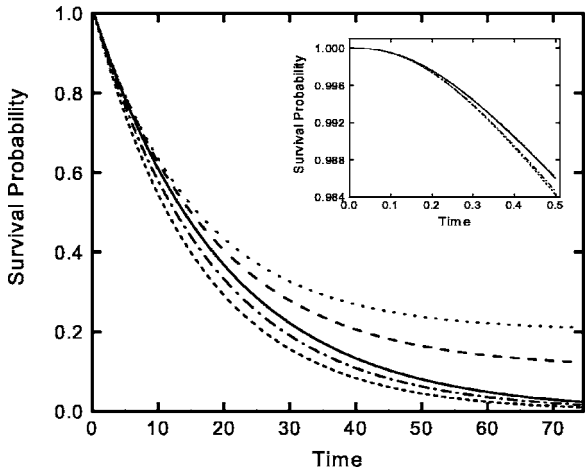


FIG. 2. The exact and optimized lower and upper bounds to the survival probability plotted against time. The one parameter upper bound (dotted line), two parameter upper bound (dashed line), one parameter lower bound (short dashed line), two parameter lower bound (dot-dashed line), and the exact (solid line) are shown. For very short time $t$, the linear behavior of survival probability for all the one and two parameter bounds as well as the exact one are shown in the inset. Note that the survival probability starts out with almost zero slope (as $\langle k\rangle \ll 1$) and then starts decreasing more rapidly. Agreement with exact calculations is found not only for small $t$ but also for large $t$. As expected, the exact survival probability lies between the bounds. The values of the parameters used were $\alpha=2$, $D=2$, $x_s=2$, $k=1.25$, and $\sigma=0.5$.

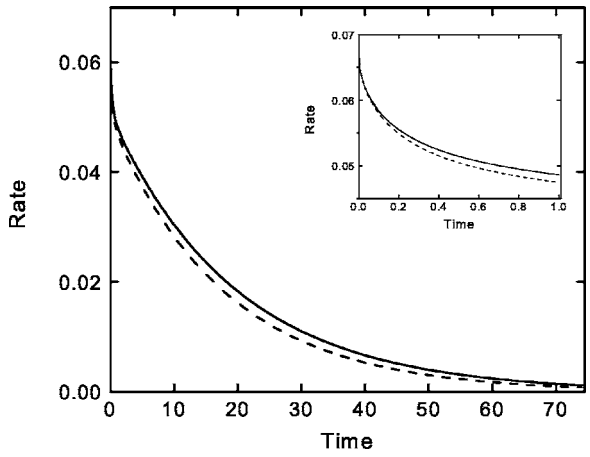


FIG. 3. The two parameter optimized lower bound (dashed line) and the exact rate (solid line) plotted against time. The inset shows the short time behavior. The values of the parameters we use were $\alpha=2$, $D=2$, $x_s=2$, $k=1.25$, and $\sigma=1$.

A measure of how good the approximations are can be obtained by calculating the mean first passage time $\tau = \int_0^\infty dT P_s(T)$: $\tau_{exact}=19.7$, $\tau_{lower}=16.08$ (for one parameter), and $\tau_{lower}=18.2$ (for two parameters) for $\sigma=1$ and $\tau_{exact}=19.95$, $\tau_{lower}=16.38$ (for one parameter), and $\tau_{lower}=18.24$ (for two parameters) when $\sigma=0.5$. As the upper bound approaches a finite value as $T\to\infty$, $\tau$ calculated from the upper bound is $\infty$.

We have calculated exact rate $R(T)$ as well as the lower bound for it given in Sec. III B and these are given in Figs. 3 and 4. In Fig. 3 it is seen that for $\sigma=1$ the rate steadily decreases with time. For $\sigma=0.5$ the rate first increases, reaches a maximum, and then decreases. This is because the initial distribution is narrow in comparison with the equilibrium one. So the probability of finding the particle at the sink position $(x_s=2)$ is very small, leading to a very small initial rate. As time passes, the probability distribution approaches

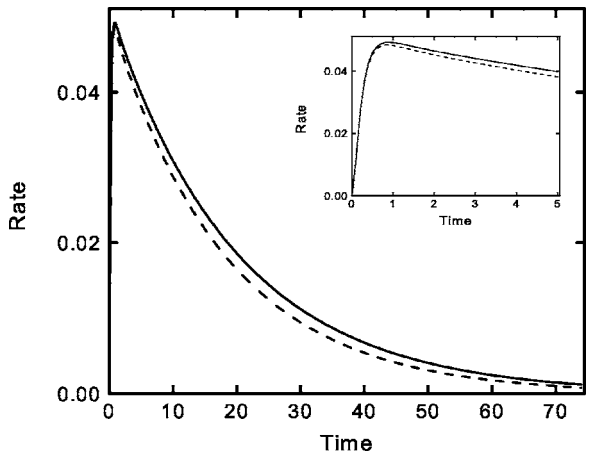


FIG. 4. The two parameter optimized lower bound (dashed line) and the exact rate (solid line) plotted against time. The short time behavior in the inset shows good agreement between the exact and approximate results. The values of the parameters used were $\alpha=2$, $D=2$, $x_s=2$, $k=1.25$, and $\sigma=0.5$.

the equilibrium one and broadens. Hence the rate increases and thus one gets a maximum in the rate. Our approximate method is able to capture this initial increase and the subsequent decrease quite well, testifying its utility.

## VI. CONCLUSIONS

To summarize, we have adopted a direct path integral approach to the calculation of survival probability in problems with dynamical disorder. Using Jensen's inequality, we have arrived at a lower bound to the survival probability. We could also get an upper bound, but it has the defect that the $T\to\infty$ limit is not correctly given. We have derived a lower bound to the rate too. Unlike the earlier approaches, our methods are in the time domain and give results for the survival probability and not its Laplace transform. Further, the inequalities are valid for arbitrary initial distribution, unlike the earlier ones which were valid only for equilibrium distributions. We have illustrated the use of the approach in a simple one dimensional problem. The method can be applied to more complex problems such as passage through a fluctuating opening,[23] loop formation in polymers,[24–27] etc. We shall report these applications in future publications.

## ACKNOWLEDGMENT

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## APPENDIX A: LONG TIME BEHAVIOR OF THE LOWER BOUND TO SURVIVAL PROBABILITY

We denote the right hand side of Eq. (7) by $P_{\text{lower}}(T)$. We show that for large $T$, $P_{\text{lower}}(T)$ decays exponentially. For this we use the operator notations of quantum mechanics. We define $\phi(x,t)=e^{V(x)/(2D)}P(x,t)$. Then $\phi(x,t)$ obeys the equation

$$\frac{\partial\phi(x,t)}{\partial t}=-\hat{H}\phi(x,t), \tag{A1}$$

where $\hat{H}$ is the "Hamiltonian" corresponding to the action $A$, given by

$$\hat{H}=-D\frac{\partial^2}{\partial x^2}+\frac{1}{2}\frac{d^2V(x)}{dx^2}-\frac{1}{4D}\left(\frac{dV(x)}{dx}\right)^2-k(x). \tag{A2}$$

Then, the path integral for survival probability can be rewritten as

$$P(T)=\langle\phi_F|e^{-T\hat{H}}|\phi_0\rangle, \tag{A3}$$

with $\phi_0(x)=e^{V(x)/(2D)}P_0(x)$ and $\phi_F(x)=e^{-V(x)/(2D)}$. Equation (4) can be written as

$$P(T)=P_{\text{tr}}(T)\frac{\langle\phi_F|e^{-T\hat{H}}|\phi_0\rangle}{\langle\phi_F|e^{-T\hat{H}_{\text{tr}}}|\phi_0\rangle}, \tag{A4}$$

where

$$P_{\text{tr}}(T)=\langle\phi_F|e^{-T\hat{H}_{\text{tr}}}|\phi_0\rangle \tag{A5}$$

is the survival probability under trial action and $\hat{H}_{\text{tr}}$ is the Hamiltonian corresponding to this trial action. In this notation,

$$\langle\Delta A[x(s)]\rangle_{A_{\text{tr}},T}=\frac{\int_0^T ds\langle\phi_F|e^{-(T-s)\hat{H}_{\text{tr}}}\Delta He^{-s\hat{H}_{\text{tr}}}|\phi_0\rangle}{\langle\phi_F|e^{-T\hat{H}_{\text{tr}}}|\phi_0\rangle}, \tag{A6}$$

where $\Delta\hat{H}=\hat{H}-\hat{H}_{\text{tr}}$. We now introduce the eigenfunctions and eigenvalues of $\hat{H}_{\text{tr}}$, which we denote as $E_{\text{tr}}^n$ and $|\psi_{\text{tr}}^n\rangle$, with $n=0,1,2\ldots$. Using the resolution of identity $\Sigma_{n=0}^{\infty}|\psi_{\text{tr}}^n\rangle\langle\psi_{\text{tr}}^n|$ we can write

$$P_{\text{tr}}(T)=\sum_{n=0}^{\infty}\langle\phi_F|\psi_{\text{tr}}^n\rangle e^{-TE_{\text{tr}}^n}\langle\psi_{\text{tr}}^n|\phi_0\rangle, \tag{A7}$$

which in the $T\to\infty$, is dominated by the first term in the sum and hence becomes

$$P_{\text{tr}}(T)\sim\langle\phi_F|\psi_{\text{tr}}^0\rangle e^{-TE_{\text{tr}}^0}\langle\psi_{\text{tr}}^0|\phi_0\rangle. \tag{A8}$$

Similarly, in the $T\to\infty$ limit,

$$\langle\Delta A[x(s)]\rangle_{A_{\text{tr}},T}\sim T\langle\psi_{\text{tr}}^0|\Delta\hat{H}|\psi_{\text{tr}}^0\rangle, \tag{A9}$$

so that

$$P_{\text{lower}}(T)\sim\langle\phi_F|\psi_{\text{tr}}^0\rangle\langle\psi_{\text{tr}}^0|\phi_0\rangle e^{-T(E_{\text{tr}}^0+\langle\psi_{\text{tr}}^0|\Delta\hat{H}|\psi_{\text{tr}}^0\rangle)}, \tag{A10}$$

showing that $P_{\text{lower}}(T)$ decays exponentially, at a rate determined by $(E_{\text{tr}}^0+\langle\psi_{\text{tr}}^0|\Delta\hat{H}|\psi_{\text{tr}}^0\rangle)=\langle\psi_{\text{tr}}^0|\hat{H}|\psi_{\text{tr}}^0\rangle$, which is nothing but a variational estimate of the lowest eigenvalue of $\hat{H}$.

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